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THE REDUCTION
OF
HYDROXYLAMINODIHYDROUMBELLULONEOXIME

BY
FRANK TUTIN

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES
FREDERICK B. POWER, PH.D., *Director*
6, King Street, Snow Hill
LONDON, E.C.

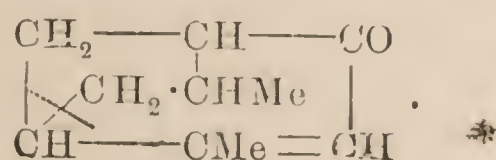
XXIX.—*The Reduction of Hydroxylaminodihydro-umbelluloneoxime.*

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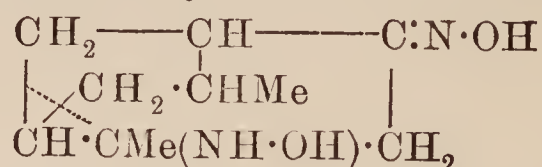
It was shown by Power and Lees (Trans., 1904, 85, 636) that when umbellulone is treated with an excess of hydroxylamine in alcoholic solution, hydroxylaminodihydroumbelluloneoxime is formed. The present author has submitted this compound to the reducing action of sodium and alcohol with the object of ascertaining the properties of the resulting basic product, and whether it consisted of a single substance or a mixture of optical isomerides, such as had been observed to be formed by the reduction of *l*-methoneoxime (Tutin and Kipping, Trans., 1904, 85, 65).

It has been shown (Lees, Trans., 1904, 85, 644) that when bromodihydroumbellulone is reduced with sodium and alcohol, and that when umbellulone itself is submitted to this treatment (Tutin, Trans., 1906, 89, 1118), one of the closed rings contained in the umbellulone molecule is opened by the addition of two atoms of hydrogen. In the preceding paper ("The Constitution of Umbellulone. Part II.") it is shown that a similar opening of the ring occurs when umbellulonic acid is reduced by the same reagent. It would therefore appear that the capability of addition of two atoms of hydrogen on treatment with sodium and alcohol is a property of that ring contained in the umbellulone molecule which is also present in umbellulonic acid. Taking this into consideration, it would appear probable that hydroxylaminodihydroumbelluloneoxime would on reduction give aminotetrahydroumbellulylamine, and not aminodihydroumbellulylamine, as might have been expected. The difference in the percentage composition of the respective salts and derivatives of these two bases is very small, and, from the results afforded by the analysis of the dihydrochloride, dibenzoate, and dibenzoyl derivative of the base obtained, it is impossible to say with certainty whether the latter has the formula $C_{10}H_{20}N_2$ or $C_{10}H_{22}N_2$. Considering all the facts, however, it is most probable that it is aminotetrahydroumbellulylamine, $C_{10}H_{22}N_2$.

It has been shown (Trans., 1906, 89, 1105, and preceding paper) that umbellulone possesses a constitution represented by the following formula:



Hydroxylaminodihydroumbelluloneoxime, being analogous in its properties to hydroxylaminodihydrocarvoneoxime (*Ber.*, 1898, 31, 1810), will therefore be represented by the following formula:



If, as appears probable, the opening of the ring on the reduction of this compound takes place at the same point as in umbellulonic acid when reduced (*loc. cit.*), namely, at the point indicated by the dotted line, then aminotetrahydroumbellulylamine will be 1:3-diamino-1-methyl-4-isopropylcyclohexane (1-aminomenthylamine),



Aminotetrahydroumbellulylamine is a liquid (b. p. 136—138°/50 mm.) possessing a not very marked basic odour. It dissolves in water with the development of heat, and has a specific rotatory power, calculated from that of its dihydrochloride, of -18.8° . The *sulphate* and Reychler's *d-camphorsulphonate* were prepared from it, but were found to be uncrystallisable, deliquescent syrups. *Aminotetrahydroumbellulylamine dibenzoate* crystallises in needles which melt at 212—213°; the *dihydrochloride* also forms needles, but it is infusible at 305°. *Dibenzoylamino-tetrahydroumbellulylamine* crystallises in prisms or in leaflets, which melt at 194°.

EXPERIMENTAL.

The hydroxylaminodihydroumbelluloneoxime used in this investigation was prepared as follows. A concentrated aqueous solution of hydroxylamine hydrochloride (62 grams) was mixed with a solution of sodium ethoxide (prepared by dissolving 20 grams of sodium in 300 c.c. of alcohol), and 34 grams of umbellulone were added. The mixture was boiled for two hours, and the greater part of the alcohol removed by distillation. After dilution with water the mixture was acidified with sulphuric acid. The undissolved oil was subsequently removed by extraction with ether, after which the acid aqueous liquid was rendered alkaline by the addition of sodium carbonate, and the hydroxylamino-oxime isolated by means of ether. The yield was 35 grams.

Aminotetrahydroumbellulylamine, $\text{C}_{10}\text{H}_{22}\text{N}_2$.—The hydroxylaminodihydroumbelluloneoxime, prepared as described above, was dissolved in 600 c.c. of absolute alcohol, and 60 grams of sodium introduced in small pieces. The mixture was not cooled, but allowed to boil vigorously. After all the sodium had dissolved, the whole was distilled with steam as long as the condensed liquid had an alkaline

reaction. The distillate, which contained some oil, was collected in hydrochloric acid, but the oil did not dissolve. When the distillation was complete, the entire acidified distillate was evaporated to a small bulk and freed from a small amount of non-basic oil by means of ether. The concentrated acid liquid was then made strongly alkaline by the addition of potassium hydroxide, when an oily liquid separated. This was extracted with ether, the ethereal liquid washed with a little water, and dried with anhydrous potassium carbonate. On removing the ether, the base was obtained as a colourless liquid, which, on distillation under 50 mm. pressure, boiled between 136° and 138° . The substance was not quite pure, but contained a very small quantity of another base. The whole of the distillate was, therefore, dissolved in a slight excess of dilute sulphuric acid, when a crystalline sulphate separated which was practically insoluble in cold water. This was collected, but amounted only to 0.2 gram; it melted at 199° . The filtrate, which contained the *aminotetrahydroumbellulylamine sulphate*, was concentrated in a vacuum, but did not crystallise, and the base was therefore again liberated.

Aminotetrahydroumbellulylamine is a liquid which readily absorbs carbon dioxide from the atmosphere. When mixed with about an equal quantity of water, considerable heat is developed and a homogeneous liquid is obtained, but on the addition of a little more water an oil separates, which, however, is redissolved on further dilution.

Aminotetrahydroumbellulylamine Dihydrochloride, $C_{10}H_{22}N_2 \cdot 2HCl$.—A portion of the base was dissolved in water, and dilute hydrochloric acid added until the liquid had an acid reaction. As it was found that dissociation occurred when this solution was heated, it was concentrated in a vacuum over sulphuric acid, when it eventually formed a hard, partly crystalline mass. This was dissolved in boiling alcohol and the solution concentrated, after which the dihydrochloride separated in colourless prisms, which, when heated to 305° , did not melt but slowly decomposed:

0.1071 gave 0.1940 CO_2 and 0.0924 H_2O . $C = 49.4$; $H = 9.6$.

0.2489 „ 25.0 c.c. of nitrogen at 22° and 760 mm. $N = 11.4$.

0.1389 „ 0.1637 $AgCl$. $Cl = 29.1$.

0.1051 „ 0.1188 $AgCl$. $Cl = 29.0$.

$C_{10}H_{20}N_2 \cdot 2HCl$ requires $C = 49.8$; $H = 9.1$; $N = 11.6$; $Cl = 29.4$ per cent.

$C_{10}H_{22}N_2 \cdot 2HCl$ „ $C = 49.4$; $H = 9.9$; $N = 11.5$; $Cl = 29.2$ „ „

The optical rotation of the dihydrochloride was determined in absolute alcohol and in water:

0.4086 dissolved in 25 c.c. of absolute alcohol gave $\alpha_D - 0^{\circ} 42'$ in a 2-dcm. tube, whence $[\alpha]_D - 21.41^{\circ}$.

0.4086 dissolved in 25 c.c. of water gave $\alpha_D - 0^\circ 26'$ in a 2-dcm. tube, whence $[\alpha]_D - 13.25^\circ$. The specific rotatory power of the base, calculated from that of the dihydrochloride is $[\alpha]_D - 18.8^\circ$.

Aminotetrahydroumbellulylamine dihydrochloride dissolves in water with great readiness; it is moderately soluble in alcohol, and almost insoluble in ethyl acetate. In a mixture of ethyl acetate and alcohol it dissolves more readily in the cold than when heated.

Aminotetrahydroumbellulylamine Dibenzoate, $C_{10}H_{22}N_2 \cdot 2C_7H_6O_2$.—To an aqueous solution of the base, a slight excess of benzoic acid was added, and on evaporation in a vacuum over sulphuric acid a hard crystalline mass was obtained. This was dissolved in boiling alcohol, and the liquid concentrated, after which the salt separated in colourless prisms which melted at $212-213^\circ$, and this melting point was not altered by further crystallisation:

0.1042 gave 0.2660 CO_2 and 0.0755 H_2O . $C = 69.6$; $H = 8.1$.

$C_{10}H_{20}N_2 \cdot 2C_7H_6O_2$ requires $C = 69.9$; $H = 7.7$ per cent.

$C_{10}H_{22}N_2 \cdot 2C_7H_6O_2$ „ $C = 69.5$; $H = 8.2$ „ „

The optical rotation of the dibenzoate was determined in water and in absolute alcohol. 0.4244, dissolved in 25 c.c. of absolute alcohol, gave $\alpha_D - 0^\circ 18'$ in a 2-dcm. tube, whence $[\alpha]_D - 8.83^\circ$. 0.4244, dissolved in 25 c.c. of water, gave $\alpha_D - 0^\circ 15'$ in a 2-dcm. tube, whence $[\alpha]_D - 7.36^\circ$. The specific rotation of the base, calculated from that of its dibenzoate, is $[\alpha]_D - 17.9^\circ$.

A quantity of the dibenzoate was fractionally crystallised from alcohol, but all the crops of crystals obtained were indentical and had a uniform melting point of $212-213^\circ$.

Dibenzoylaminotetrahydroumbellulylamine, $C_{10}H_{20}N_2(CO \cdot C_6H_5)_2$.—The base obtained from either the pure dibenzoate or the pure dihydrochloride, when benzoylated by means of the Schotten-Baumann method, gave a product which, when crystallised from alcohol, melted at 194° . On fractional crystallisation this was found to be homogeneous.

0.0990 gave 0.2762 CO_2 and 0.0691 H_2O . $C = 76.1$; $H = 7.8$.

0.2642 „ 16.6 c.c. of nitrogen at 20° and 776 mm. $N = 7.3$.

$C_{10}H_{18}N_2(CO \cdot C_6H_5)_2$ requires $C = 76.6$; $H = 7.4$; $N = 7.4$ per cent.

$C_{10}H_{20}N_2(CO \cdot C_6H_5)_2$ „ $C = 76.2$; $H = 7.9$; $N = 7.4$ „ „

The optical rotation of the dibenzoyl derivative was determined in chloroform solution. 0.5379, dissolved in 25 c.c. of chloroform, gave $\alpha_D + 5^\circ 3'$ in a 2-dcm. tube, whence $[\alpha]_D + 117.3^\circ$.

Dibenzoylaminotetrahydroumbellulylamine is readily soluble in chloroform and nearly insoluble in water. When crystallised from absolute alcohol, in which it is moderately soluble, it separates in short

stout prisms, but from dilute alcohol it is obtained in long leaflets; occasionally both forms of crystals are simultaneously deposited.

As the most readily soluble portions obtained by the fractional crystallisation of the dibenzoate and the dihydrochloride did not crystallise with facility, the base which they contained was benzoylated and the resulting dibenzoyl derivative submitted to a systematic process of fractional crystallisation. The only substance which could be obtained in a state of purity from this was the dibenzoyl derivative melting at 194° , and this represented by far the greater part of the material. Nevertheless, the two most readily soluble fractions were oily in character, and were evidently mixtures, as they could only with difficulty be induced to crystallise. The substances contained in these mixtures, other than the benzoyl derivative described, were probably benzoyl derivatives of bases stereoisomeric with aminotetrahydroumbellulylamine, but they were present in so small an amount that their isolation was impossible without employing a very much larger quantity of material than was available.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.



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